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The Crystal Structure of 3,3′-Trithiobis-(2,4-pentanedione)

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The crystal structure of 3,3′-trithiobis-(2,4-pentanedione), $C_{10}H_{14}O_4S_3$, has been determined by X-ray diffraction methods. The crystals are orthorhombic, space group *Pbcn* and the unit cell contains four molecules and has dimensions $a=13{\cdot}12$ (3), $b=9{\cdot}35$ (2) and $c=11{\cdot}03$ (3) Å. The structure was solved by the heavy-atom method and refined by full-matrix least-squares to a final R index of 5·8% for 856 observed reflexions. Hydrogen atoms were located by a difference Fourier synthesis. The 2,4-pentanedione residue is planar and there is evidence for double-bond localization in it. The O(1)···O(2) distance is 2·46 Å, indicating a strong hydrogen bond. The S(1)–S(2) bond distance is $2{\cdot}083 \pm 0{\cdot}006$ Å while S(2)–C(3) is $1{\cdot}802 \pm 0{\cdot}012$ Å. The dihedral angle, S–S–S/S–S–C, is 73·2°.

Introduction

Reaction of sulfur chlorides (SCl_2, S_2Cl_2) with acetylacetone results in the formation of bis-(β-diketones) of the type shown in Fig. 1. On the basis of infrared and proton magnetic resonance spectra (Dewar, Ferguson, Hentschel, Wilkins & Williams, 1964), the compounds for which $n=1,2$ have been shown to be enolized with the formation of an intramolecular hydrogen bond. The crystal structure analysis of the compound for which $n=3$ has been undertaken to determine the stereochemistry about the trisulfide group and the nature of the acetylacetone residue.

Experimental

3,3′-Trithiobis-(2,4-pentanedione) was prepared by allowing a solution of S_2Cl_2 and acetylacetone in CCl_4 to evaporate to dryness at room temperature. The compound was purified by recrystallization from acetone and crystals, suitable for X-ray analysis, were grown from acetone.

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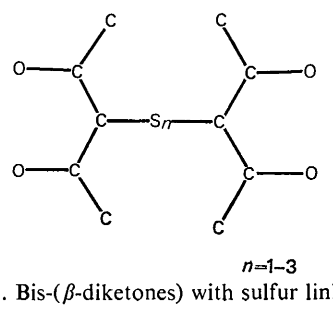

n=1–3

Fig. 1. Bis-(β-diketones) with sulfur linkages.

The lattice constants were determined from zero-level Weissenberg photographs, taken about each crystallographic axis with Cu $K\alpha$ radiation. Density measurements were made by flotation in potassium iodide solutions.

Crystal data

3,3′-Trithiobis-(2,4-pentanedione)
$C_{10}H_{14}O_4S_3$, m.p. 133–134°C, M.W. 294·4;
Orthorhombic;
$a=13{\cdot}12 \pm 0{\cdot}03$, $b=9{\cdot}35 \pm 0{\cdot}02$, $c=11{\cdot}03 \pm 0{\cdot}03$ Å;
$V=1353{\cdot}1$ Å^3;
$D_m=1{\cdot}49$ g.cm^{-3}, $D_c=1{\cdot}45$ g.cm^{-3};
$Z=4$, $F(000)=616$;
$\mu=50{\cdot}4$ cm^{-1} for Cu $K\alpha$ radiation;

Absent spectra, $0kl$ when k is odd, $h0l$ when l is odd, $hk0$ when $h+k$ is odd, ($h00$ when h is odd, $0k0$ when k is odd, $00l$ when l is odd);
Space group, *Pbcn* (No. 60, *International Tables for X-ray Crystallography*, 1969).

Intensity data were collected from equi-inclination Weissenberg photographs with the use of Cu $K\alpha$ radiation and a multiple-film technique with visual intensity estimation against a set of timed exposures of a single reflexion. Eight layers on the c axis ($l=0$ to 7) and four layers on the a axis ($h=0$ to 3) for cross correlation were recorded. The crystal used measured approximately $0{\cdot}2 \times 0{\cdot}2 \times 0{\cdot}2$ mm. The intensities were corrected for Lorentz and polarization factors. No absorption correction was applied. An overall scale factor and isotropic temperature factor were determined by the method of Wilson (1942).

Structure determination and refinement

For space group *Pbcn*, there are eight general positions in the unit cell. Since the density indicates four molecules of $C_{10}H_{14}O_4S_3$ per unit cell, each molecule must consist of two asymmetric units symmetrically disposed about a special position. Trisulfides do not generally have a centre of symmetry but a twofold axis is common (Dawson, Mathieson & Robertson, 1948). The trisulfide group was assumed to be unbranched with the middle sulfur atom lying on a twofold axis, parallel to the *b* axis, at the special positions (4*c*) (*International Tables for X-ray Crystallography*, 1969).

A three-dimensional Patterson synthesis allowed the location of both sulfur atoms, one as expected on the twofold axis. Series of structure factor calculations and Fourier syntheses revealed the position of all non-hydrogen atoms. The *R* index* at this stage was 30·8 %.

Block-diagonal least-squares refinement,† with isotropic temperature factors assigned to each atom and unit weight for each reflexion, reduced *R* to 15·1 %. Because S(1) has some symmetry-fixed parameters (Levy, 1956; Peterse & Palm, 1966), none of its parameters were varied, due to a restriction imposed by the S.P.S. computer program used. Refinement was continued with anisotropic temperature factors for the atoms [S(1) parameters were fixed].

Full-matrix least-squares refinement, with anisotropic temperature factors of the form $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$, unit weight for each reflexion and anomalous dispersion correction for the sulfur atoms, including both real and imaginary parts ($\Delta f'$ and $\Delta f''$), reduced *R* to 8·8 %. The parameters of S(1) which were not symmetry fixed were allowed to vary. A difference Fourier synthesis at this stage located all hydrogen atoms and two further cycles of refinement, with hydrogen atoms given the temperature factors of the atoms to which they were attached (only hydrogen positions were varied), gave a final *R* and weighted *R* of 5·8 % and 6 % respectively for observed reflexions. If unobserved reflexions were included, with $F_o=\frac{1}{2}F_{\min}$ for each layer, *R* was 7·3 %

Scattering factors for sulfur, carbon and oxygen atoms were taken from the tables of Cromer & Waber (1965), those for hydrogen atoms from the table of Stewart, Davidson & Simpson (1965) while anomalous dispersion corrections for sulfur atoms, with Cu *Kα* radiation, were taken from *International Tables for X-ray Crystallography*(1962).

* $R=\frac{\sum(||F_o|-|F_c||)}{\sum|F_o|}$.

† Block-diagonal least-squares were calculated with the program of G.A. Mair for the IBM 1620 computer.

Full-matrix least squares, on an IBM 7090 computer, were calculated with *ORFLS* (Busing, Martin & Levy, 1962).

Fourier syntheses were calculated with the program of R. Shiono for the IBM 1620 computer.

Discussion

Final values for the atomic coordinates are shown in Table 1 while temperature factors for the non-hydrogen atoms are listed in Table 2. Bond lengths and bond angles are shown in Tables 3 and 4 and in Fig. 2. A listing of the F_o and F_c values is shown in Table 5.

Table 1. *Fractional coordinates with e.s.d.'s in parentheses*

	x	*y*	*z*
S(2)	0·0061 (1)	0·1488 (1)	0·0983 (1)
S(1)	0·0000	0·2818 (2)	0·25
C(1)	0·1906 (4)	−0·0324 (6)	0·2029 (7)
C(2)	0·2134 (4)	0·0777 (5)	0·1042 (6)
C(3)	0·1361 (3)	0·1652 (5)	0·0475 (5)
C(4)	0·1586 (4)	0·2640 (6)	−0·0390 (5)
C(5)	0·0839 (4)	0·3583 (7)	−0·1101 (7)
O(1)	0·3055 (3)	0·0972 (4)	0·0741 (4)
O(2)	0·2541 (3)	0·2784 (5)	−0·0761 (4)
H(00)	0·287 (4)	0·198 (6)	−0·016 (6)
H(11)	0·174 (4)	0·057 (5)	0·275 (5)
H(12)	0·253 (4)	−0·089 (5)	0·217 (5)
H(13)	0·135 (4)	−0·092 (6)	0·183 (6)
H(51)	0·066 (3)	0·465 (6)	−0·060 (5)
H(52)	0·019 (4)	0·293 (5)	−0·131 (5)
H(53)	0·116 (4)	0·398 (6)	−0·196 (5)

Hydrogen atoms are labelled according to the number of the carbon atom to which they are bonded. H(00) is the enol hydrogen.

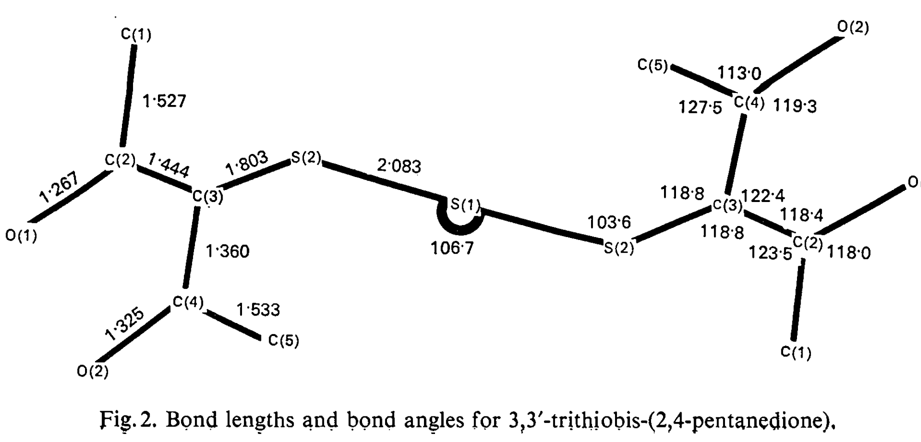

Fig. 2. Bond lengths and bond angles for 3,3′-trithiobis-(2,4-pentanedione).

Table 2. *Anisotropic temperature factors with e.s.d.'s in parentheses*

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(2)	0·0027 (5)	0·0140 (2)	0·0076 (2)	−0·0013 (1)	0·0002 (1)	−0·0008 (1)
S(1)	0·0046 (1)	0·0086 (2)	0·0098 (2)	0·0	0·0021 (1)	0·0
C(1)	0·0053 (3)	0·0072 (7)	0·0131 (9)	0·0005 (4)	−0·0014 (4)	0·0011 (6)
C(2)	0·0043 (3)	0·0076 (6)	0·0084 (7)	0·0006 (3)	−0·0001 (3)	−0·0024 (5)
C(3)	0·0030 (2)	0·0107 (7)	0·0053 (6)	−0·0010 (3)	−0·0000 (3)	−0·0021 (5)
C(4)	0·0041 (3)	0·0109 (7)	0·0045 (6)	−0·0003 (4)	−0·0003 (3)	−0·0008 (5)
C(5)	0·0043 (3)	0·0137 (9)	0·0108 (9)	−0·0004 (5)	−0·0011 (4)	0·0024 (7)
O(1)	0·0037 (2)	0·0149 (6)	0·0085 (5)	0·0017 (3)	0·0012 (2)	−0·0001 (4)
O(2)	0·0035 (2)	0·0129 (6)	0·0118 (5)	−0·0008 (3)	0·0020 (3)	0·0013 (4)

Table 3. *Bond lengths*

	Distance	E.s.d.
S(1)–S(2)	2·083 Å	0·006 Å
S(2)–C(3)	1·803	0·012
C(1)–C(2)	1·527	0·020
C(2)–C(3)	1·444	0·017
C(3)–C(4)	1·360	0·017
C(4)–C(5)	1·533	0·020
C(2)–O(1)	1·267	0·017
C(4)–O(2)	1·325	0·017
O(1)–O(2)	2·461	0·015
O(1)–H(00)	1·39	
O(2)–H(00)	1·09	
C(1)–H(11)	1·17	
C(1)–H(12)	0·99	
C(1)–H(13)	0·95	
C(5)–H(15)	1·16	
C(5)–H(25)	1·07	
C(5)–H(35)	1·10	

Table 4. *Bond angles*

	Angle	E.s.d.
S(2)–S(1)—S(2)	106·7°	0·2°
S(1)–S(2)—C(3)	103·6	0·2
S(2)–C(3)—C(2)	118·8	0·4
S(2)–C(3)—C(4)	118·8	0·4
C(1)–C(2)—C(3)	123·5	0·5
C(2)–C(3)—C(4)	122·4	0·5
C(3)–C(4)—C(5)	127·5	0·5
C(1)–C(2)—O(1)	118·0	0·5
C(3)–C(2)—O(1)	118·4	0·5
C(5)–C(4)—O(2)	113·0	0·5
C(3)–C(4)—O(2)	119·3	0·5
C(2)–O(1)—H(00)	97·0	
C(4)–O(2)—H(00)	97·0	
O(1)–H(00)–O(2)	165·4	

The *c*-axis projection (Fig. 3) shows that the configuration of the acetylacetone residues is *trans* with respect to the trisulfide grouping. Abrahams (1956) has postulated that such a configuration results if the dihedral angle at the sulfur group is less than 90°. For this compound, S–S–S/S–S–C is 73·2°.

The S(1)–S(2) bond length is the value for a single bond (Abrahams, 1956). However, the bond is longer than that expected for a dihedral angle of 73·2° (Hordvik, 1966), for which a value of 2·05 Å is anticipated. The S–S–S and S(1)–S(2)–C(3) bond angles and the S(2)–C(3) bond length are within the accepted range (Abrahams, 1956).

For the acetylacetone residue, a least-squares plane has been calculated. The equation to this plane is

$$0{\cdot}1126X+0{\cdot}7047Y+0{\cdot}7004Z=1{\cdot}645\,.$$

Table 5. *Observed and calculated structure factors*

The first column contains the running index *h*, the second $F_o(\times 10)$, the third $F_c(\times 10)$, the fourth $A_c(\times 10)$ and the fifth $B_c(\times 10)$ (due to anomalous dispersion). Unobserved reflexions are shown by *.

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Deviations of atoms from this plane are shown in Table 6. In the acetylacetone group, C(2)–O(1) is near the value for a carbon–oxygen double bond (1·23 Å) and C(4)–O(2) is intermediate in length between that for a double and that for a single bond (1·43 Å). A similar bond length relationship exists between C(4)–C(3) and C(2)–C(3). From these relationships, it is evident that double-bond localization exists in the enolized ring. Similar results were obtained for dibenzoylmethane (Williams, 1966) and bis-(*m*-chlorobenzoyl)methane (Engebretson & Rundle, 1964). Consistent with this picture of the enol ring, the enol hydrogen H(00), is attached to O(2). The O(2)–H(00) and O(1)···H(00) distances of 1·09 and 1·39 Å seem to be significantly different. The O(1)–H(00)–O(2) bond angle is nearly linear, 165·4°.

Table 6. *Deviation of atoms from least-squares plane*

	Distance
C(1)	−0·0108 Å
C(2)	−0·0132
C(3)	0·0111
C(4)	0·0272
C(5)	−0·0102
O(1)	0·0187
O(2)	−0·0227
S(2)	0·1029*
H(00)	−0·0358*

* Atom not included in least-squares plane calculation.

A neutron structure determination of this compound currently refined to an R index of 0·068 % produced bond lengths O(2)–H(00) and O(1)···H(00) of 1·17(2) and 1·39(2) with fractional coordinates of H(00) of 0·298(1), 0·203(2) and −0·012(1) agreeing well with those shown in Table 1.

The O(1)···O(2) contact is short (2·461 Å). This value is comparable with values found for other enolized β-diketones. In dibenzoylmethane, bis-(*m*-chlorobenzoyl)methane and bis-(*m*-bromobenzoyl)methane (Williams, Dumke & Rundle, 1962), the values are 2·468, 2·475 and 2·464 Å respectively. Formation of such a short oxygen–oxygen contact is due to the steric effect of S(2). Pauling (1960) gives the van der Waals approach of carbon to sulfur as 3·85 Å. For this compound S(2)···C(1) and S(2)···C(5) are 3·17 and 3·18 Å, resulting in strain in the acetylacetone residue. Relief of some of this strain is evidenced by the large C(5)–C(4)–C(3) and C(1)–C(2)–C(3) bond angles, the short O(1)···O(2) contact and the larger β_{33} for O(1), O(2), C(1), C(5) (β_{33} is nearly perpendicualr to the plane of acetylacetone). The interposition of a hydrogen between O(1) and O(2) reduces the coulombic repulsion, a result of the close approach of the oxygen atoms.

The closest non-bonded contact of two sulfur atoms is 3·53 Å which is less than the value of Pauling. However similar van der Waals contacts have been recorded for 2,2′-di-iododiethyl trisulfide (Donohue, 1950) and 2-thiohydantoin (Walker, Folting & Merritt, 1969).

A neutron structure determination of this compound is being undertaken to verify the evidence for double-bond localization and the position of H(00).

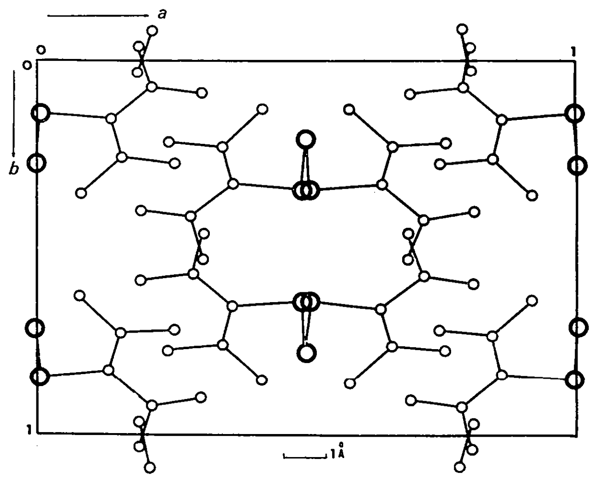

Fig. 3. *c* axis projection of 3,3′-trithiobis-(2,4-pentanedione).

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